Effect of Thermo-Mechanical Treatment on Electrical Conductivity and Strength of Cu–0.29 mass%Zr Alloy Wires^{*1}

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In our previous study, a thin wire of a Cu–0.29 mass%Zr alloy produced by repeated intermediate annealing during rolling and wire-drawing (IA wire) exhibited a 0.2% proof stress, $\sigma_{0.2}$, of 600 MPa, an ultimate tensile strength, σ_u , of 630 MPa, and an electrical conductivity, E , of 91.7%IACS. A thin wire of the alloy produced by ECAP-conform processing and subsequent rolling and wire-drawing (ECAP wire) showed larger values of $\sigma_{0.2} = 730$ MPa and $\sigma_u = 790$ MPa but a smaller value of $E = 73.0\%$ IACS than the IA wire. This study investigates the causes of the lower value of E and the higher value of $\sigma_{0.2}$ of the ECAP wire, and the higher value of E of the IA wire. The higher value of $\sigma_{0.2}$ of the ECAP wire is attributed to its smaller grain size and higher dislocation density. The lower value of E of the ECAP wire is primarily attributable to the fact that newly found, ordered face-centered cubic (fcc) precipitates having a cube-on-cube orientation relationship to the Cu matrix in the alloy produced by the ECAP-conform processing were cut by dislocations during rolling and wire drawing, resulting in dissolution in the Cu matrix. The IA wire showed the higher value of E because recrystallization by repeated intermediate annealing changed all the fcc precipitates into incoherent fcc precipitates that were not cut by dislocations. Further, based on the obtained results, an attempt was made to fabricate thin wires of the alloy having good strength, ductility and electrical conductivity. All the fcc precipitates in the alloy were made incoherent with the Cu matrix by utilizing recrystallization after sufficient precipitation. Then the alloy was processed by ECAP and subsequently wire-drawn. The fabricated thin wire exhibited higher values of $\sigma_u = 820$ MPa, $\varepsilon_t = 4.0\%$ and $E = 86.9\%$ IACS. [doi:10.2320/matertrans.MT-D2021001]

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1. Introduction

In recent years, Cu alloy wires used for electronic components have become extremely thinner. As a result, strength enough to prevent breakage and high electrical conductivity are required for Cu alloy wires. Tin-plated soft Cu wires and dilute Cu–Cr alloy wires¹⁾ with electrical conductivities, E , of 85–90%IACS have been proposed as wires with high electrical conductivity so far. However, their tensile strengths, σ_u , ranging from 200 to 450 MPa are insufficient.

Recently, Muramatsu *et al.* have conducted a series of studies on the mechanical properties of drawn wires of hypoeutectic Cu–0.72–7.2 mass%Zr alloys (hereinafter mass% will be omitted in the notation).²⁾ Muramatsu *et al.* reported that the Cu–7.2Zr alloy wire with a drawing ratio, η , of 8.6 had a high tensile strength, σ_u , of 2.2 GPa and the Cu–0.72Zr alloy wire with $\eta = 9.4$ had a high electrical conductivity, E , of 83%IACS.²⁾

Applications such as power transmission cables require a high electrical conductivity of 90%IACS or higher. For improving the electrical conductivity of Cu–Zr wires further, Muramatsu *et al.* conducted repeated intermediate annealing during rolling and subsequent wire drawing, followed by final wire drawing for a Cu–Zr alloy produced by vertical upward continuous casting (VUCC) with a low Zr

concentration of 0.29 (0.2 at%).³⁾ As a result, a Cu–Zr wire having properties of a tensile strength, σ_u , of 630 MPa, a total elongation, ε_t , of 1.1%, and an electrical conductivity, E , of 91.7%IACS was obtained. On the other hand, the wire produced by rolling of the as-cast Cu–Zr alloy and subsequent annealing, followed by rolling and wire drawing without intermediate annealing, showed $\sigma_u = 820$ MPa, $\varepsilon_t = 1.5\%$, and $E = 78.2\%$ IACS. In other words, the wire subjected to intermediate annealing possessed the higher value of E , but the lower value of ε_t despite the lower value of σ_u .

In the previous paper,⁴⁾ ECAP-conform processing, which was one of the severe plastic deformation, was introduced prior to rolling and subsequent wire drawing of the Cu–0.29Zr alloy in order to improve the strength and ductility by grain refinement. The ECAP-conform processing enhanced the degree of grain refinement, resulting in a grain size of 120 nm of the Cu–0.29Zr alloy after subsequent tandem rolling followed by wire drawing. This grain size was finer than that of 180 nm of the Cu–0.29Zr alloy wire produced without the ECAP-conform processing. Although a good strength, σ_u , of 790 MPa and a ductility, ε_t , of 3.9% were achieved by introducing the ECAP-conform processing, the electrical conductivity, E , decreased from 88%IACS to 73%IACS before and after the wire drawing. However, the reason for the decrease in electrical conductivity by wire drawing was not elucidated.

In the present study, detailed microstructural observations were performed on the Cu–0.29Zr alloy subjected to different processing routes: 1. round-bars subjected to ECAP-conform processing, 2. wires subjected to ECAP-conform processing with subsequent rolling and wire drawing, and 3. wires

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subjected to intermediate annealing with high electrical conductivity. Through these experiments, the following three unclear points were examined: (1) the reason for the decrease in electrical conductivity by the rolling and wire drawing after the ECAP-conform processing, (2) the reason for the high strength of the wire after the rolling and wire drawing, and (3) the reason for the high electrical conductivity of the wire subjected to the intermediate annealing. Furthermore, based on the obtained results, an attempt was made to produce an alloy wire with a good balance of strength, ductility, and electrical conductivity.

2. Experimental Procedures

The processing routes for the ECAP-conform processing of Cu–0.29Zr alloy round-bars with a diameter, d , of 14 mm produced by VUCC and subsequent tandem rolling followed by wire drawing have already been described in the previous paper.⁴⁾ First, a cast round-bar was subjected to conform extrusion from $d = 14$ mm to 10 mm, followed by ECAP-conform processing for four times. Then, the round-bar was tandem-rolled to $d = 3$ mm and machined to $d = 2.7$ mm. This machined specimen before being subjected to wire drawing is referred to as “ECAP specimen”. The wires produced by wire drawing from $d = 2.7$ mm to 0.6 mm or 0.2 mm are referred to as “0.6ECAP wire” and “0.2ECAP wire”, respectively. In addition, a cast round-bar with $d = 10$ mm without ECAP-conform processing was annealed at 650°C for 1 h, and then subjected to rolling and subsequent wire drawing to $d = 0.2$ mm⁴⁾ for comparison. The specimen before being subjected to wire drawing is referred to as “A specimen”. The wires with annealing are referred to as “A wire”. Especially, the wires subjected to wire drawing to $d = 0.6$ or 0.2 mm are expressed as “0.6A wire” and “0.2A wire”, respectively.

Furthermore, referring to the processing route for producing wires with intermediate annealing in the previous study,³⁾ cast round-bars with $d = 10$ mm were tandem-rolled to $d = 5$ mm, and then annealed at 650°C for 1 h. After that, the wires with $d = 1$ mm were obtained by repeated wire drawing and subsequent intermediate annealing at 650°C for 1 h for three times. This wire before being subjected to subsequent final wire drawing is referred to as “IA specimen”. Besides, the wires subjected to the final wire drawing are referred to as “IA wire”. Specifically, the wires subjected to the final wire drawing to $d = 0.6$ or 0.2 mm are referred to as “0.6IA wire” and “0.2IA wire”, respectively.

Microstructural observations were carried out using a transmission electron microscope (TEM: Tecnai G² 30, FEI, Hillsboro, OR, USA) and a field-emission scanning electron microscope (FE-SEM: JSM-7100F, JEOL, Tokyo, Japan). TEM specimens were prepared as follows. In the case of specimens of the alloy before being subjected to wire drawing, disk-shaped specimens with a diameter of 3 mm were cut out from the alloy along the longitudinal section. Then, the disk-shaped specimens were polished to a thickness of 0.2 mm, and subsequently electro-polished using a solution of 20% nitric acid and 80% methanol at a temperature of about –60°C and a voltage of 4.0 V. On the other hand, in the case of the drawn wires, wires with a

diameter, d , of 0.6 mm were used for TEM microstructural observations due to the difficulty in preparing TEM specimens of the wires with a diameter, d , of 0.2 mm. First, the 0.6 mm wires were cut to an appropriate size, followed by polishing into strips with a thickness of 100 μ m. Then, ion beam processing was carried out using an ion slicer (EM-09100IS, JEOL, Tokyo, Japan) at a voltage of 5.0 kV.

Tensile tests were performed using a universal testing machine (AUTOGRAPH AG-X, Shimadzu, Kyoto, Japan) for the alloy specimens before being subjected to wire drawing. Flat tensile specimens having shoulders and a gauge section with a gauge length of 5 mm, a gauge width of 3 mm, and a thickness of 0.3 mm were cut from the round-bars and tested. The drawn wires were tensile-tested using a universal testing machine (AUTOGRAPH AG-I, Shimadzu, Kyoto, Japan) with a distance of 100 mm between the grippers.

To evaluate the dislocation density, X-ray diffraction (XRD) experiments were performed using an X-ray diffractometer (RINT-2500, Rigaku Corporation, Tokyo, Japan) with Cu-K α radiation. The dislocation densities were estimated by converting the amount of strain calculated from the full widths at half maximum (FWHM) of the X-ray diffraction peaks corresponding to the (111), (200), (220), and (311) planes by the modified Williamson-Hall method.⁵⁾

The electrical conductivities were determined as $E = (\rho_0/\rho) \times 100$ using a resistivity, ρ_0 , of pure copper ($\rho_0 = 17.2$ n Ω m) and a measured resistivity, ρ , by the four-terminal method.

3. Results

3.1 Mechanical properties and electrical conductivities

Table 1 lists the 0.2% proof stress $\sigma_{0.2}$, σ_u , ϵ_t , and E of the 0.2ECAP, 0.2A, and 0.2IA wires. The data for the 0.2ECAP and 0.2A wires were taken from the previous study.⁴⁾ Not only the values of $\sigma_{0.2}$ and σ_u but also the value of ϵ_t of the 0.2ECAP wire was higher than those of the 0.2A wire. The 0.2IA wire possesses the lowest ductility in the three wires despite the lowest strength. The reason for the low ductility of the 0.2IA wire will be reported in another paper.

The electrical conductivity of the cast alloy was 76.0%IACS, while those of the ECAP, A, and IA specimens before wire drawing were 88.2, 88.9, and 93.3%IACS, respectively. Thus, the values of E of the ECAP, A, and IA specimens were higher than that of the cast alloy. The electrical conductivities of the 0.2ECAP, 0.2A, and 0.2IA wires decreased to 73.0, 74.1, and 90.5%IACS, respectively, as shown in Table 1, due to the subsequent rolling and wire

Table 1 0.2% proof stress, $\sigma_{0.2}$, ultimate tensile strength, σ_u , total elongation, ϵ_t , and electrical conductivity, E , for the 0.2ECAP, 0.2A, 0.2IA and 0.2IM wires.

Specimen	$\sigma_{0.2}$ (MPa)	σ_u (MPa)	ϵ_t (%)	E (%IACS)
0.2ECAP	730	790	3.9	73.0
0.2A	650	710	2.9	74.1
0.2IA	580	610	1.2	90.5
0.2IM	770	820	4.0	86.9

drawing. While the electrical conductivity of the 0.2IA wire hardly decreased, the decrease in electrical conductivity of the 0.2ECAP and 0.2A wires was significant. The 0.2IM wire shown in Table 1 will be explained in Section 4.3.

3.2 Microstructures

The grain size, D , of the cast alloy was $13\ \mu\text{m}$. Granular eutectics consisting of Cu and Cu_5Zr with an average diameter of about $1.5\ \mu\text{m}$ were observed inside the grains, while plate-shaped eutectics with a length of about $10\ \mu\text{m}$ were seen at the grain boundaries.

In addition, inside the grains of the cast alloy, there were fine spherical precipitates clearly observed by the dark-field TEM imaging rather than the bright-field imaging. Figure 1(a) shows a dark-field TEM image of spherical precipitates taken using a reflection spot of the precipitates. Figure 1(b) is the $[110]_{\text{Cu}}$ selected-area diffraction pattern (SADP) corresponding to (a). The average diameter of the spherical precipitates was about $12\ \text{nm}$. In Fig. 1(b), reflection spots of the precipitates can be seen near all of the spots of the Cu matrix between the transmitted spot and the Cu reflection spots. An analysis of the reflection spots of the precipitates using the lattice constant of pure Cu ($a = 0.3615\ \text{nm}$) revealed that the precipitates had a cube-on-cube orientation relationship with the Cu matrix and a lattice constant, a , of $0.42\ \text{nm}$. The subscript for the reflection spots of the precipitates having the cube-on-cube orientation relationship with the Cu matrix is written as CP. It can be judged that the precipitates are coherent or semi-coherent with the Cu matrix. Hereafter, these precipitates are referred to as coherent face-centered cubic (fcc) precipitates (or phase). In Fig. 1(b), the reflection spots of $1\bar{1}0_{\text{CP}}$ and $\bar{1}10_{\text{CP}}$ of the coherent fcc precipitates, indicated by the arrows, are

Fig. 1 (a) Dark-field TEM image of fcc precipitates in an as-cast Cu–0.29 mass%Zr alloy, (b) $[110]_{\text{Cu}}$ selected-area diffraction pattern (SADP) corresponding to (a).

also observed, indicating that the fcc phase is an ordered structure. This ordered fcc phase does not have the same lattice constant as the Cu_5Zr phase with the fcc lattice system existing on the Cu side in the Cu–Zr binary phase diagram,⁶⁾ and its structure is also different from that of the $\text{Cu}_{51}\text{Zr}_{14}$ phase around the Cu-rich corner of the phase diagram. Furthermore, the fcc ordered phase has not been reported as a GP zone or an intermediate phase as well. Thus, this fcc phase was newly found for the first time in the present study.

As in the previous paper,⁴⁾ recrystallized grains were observed in the specimens after conform extrusion as well as in the specimens after ECAP-conform processing for four times. Besides, it was confirmed that the grain size of the ECAP specimen (subjected to ECAP-conform processing for four times) was refined to $0.9\ \mu\text{m}$. Figure 2(a) and (b) depict a bright-field TEM image of spherical precipitates and a dark-field TEM image of the coherent fcc precipitates within the same recrystallized grain in the ECAP specimen. Figure 2(c) is the $[110]_{\text{Cu}}$ SADP corresponding to (a). The spherical precipitates in the recrystallized grain had an average size of about $10\ \text{nm}$. In Fig. 2(c), it can be seen that reflection spots of these precipitates, such as $1\bar{1}1_{\text{IP}}$, are observed at different

Fig. 2 (a) Bright-field TEM image of incoherent fcc precipitates inside a grain in an ECAP specimen, (b) dark-field TEM image of fcc precipitates in the same grain as in (a), (c) $[110]_{\text{Cu}}$ SADP corresponding to (a).

positions from the fcc precipitates. Analyses of many SADPs revealed that the precipitates had the same lattice constant of 0.42 nm and the same ordered structure as the fcc precipitates, but were incoherent with the Cu matrix. It was found that recrystallization during conform extrusion or ECAP-conform processing changed the coherent fcc precipitates into the incoherent fcc precipitates. The subscripts of the reflection spots for the incoherent precipitates were denoted as IP. As shown in Fig. 2(b), fine fcc precipitates, which were newly precipitated after recrystallization, with an average size of about 7 nm were also found in the recrystallized grains. In addition to the incoherent precipitates, as shown in Fig. 2(b), the fine coherent fcc precipitates newly formed after recrystallization and having an average size of about 7 nm coexisted in the recrystallized grains. Grains with the coherent and incoherent fcc precipitates accounted for about 80% of the observed grains. In the other 20% of the grains, only the incoherent fcc precipitates with an average size of about 11 nm were observed. The coherent fcc precipitates became incoherent during the grain-refinement process from $D = 13 \mu\text{m}$ in the cast alloy to $0.9 \mu\text{m}$ after ECAP-conform processing for four times. On the other hand, the grain size of the A specimen prepared for comparison was $13 \mu\text{m}$, and the average size of the coherent fcc precipitates was about 11 nm.

The grain size of the IA specimen was $5 \mu\text{m}$. In the intermediate process, recrystallization occurred by repeated intermediate annealing after rolling or wire drawing, and the coherent and incoherent fcc precipitates coexisted in the recrystallized grains. After final annealing, the coherent fcc precipitates were no longer observed in the recrystallized grains of the IA specimens, and only the incoherent fcc precipitates were present.

Subsequent rolling and wire drawing to $d = 0.6 \text{ mm}$ resulted in the formation of the incoherent fcc precipitates as well as grain refinement. In the 0.6ECAP wire, the grains having both the coherent fcc precipitates with an average size of about 9 nm and the incoherent fcc precipitates with an average size of about 10 nm and the grains having only the incoherent fcc precipitates with an average size of 11 nm were observed at a ratio of about 7:3. In the 0.6A wire, the grains having only the coherent precipitates with an average size of about 12 nm and the grains having only the incoherent precipitates with an average size of about 11 nm were observed at a ratio of about 6:4. In the 0.6IA wire, only the incoherent precipitates were confirmed in all of the observed grains.

Table 2 lists the grain size, D , of the 0.2ECAP and 0.2A wires, reported in the previous paper,⁴⁾ and the 0.2IA wire.

Table 2 Average grain size, D , and dislocation density, ρ_d , for the 0.2ECAP, 0.2A and 0.2IA wires, and precipitate radius, $\bar{r}_{ci}$, volume fraction, f_c , and inter-precipitate spacing, λ , for the 0.6ECAP, 0.6A and 0.6IA wires.

Specimen	D (nm)	ρ_d ($\times 10^{15} \text{ m}^{-2}$)	$\bar{r}_{ci}$ (nm)	f_{ci} ($\times 10^{-3}$)	λ (nm)
0.2(0.6)ECAP	120	2.0	5.0	9.3	67
0.2(0.6)A	180	1.8	5.6	10.3	69
0.2(0.6)IA	240	1.5	6.7	13.9	71

The grains were elongated along the wire drawing direction, and the grain boundary spacing parallel to the wire drawing direction was defined as D . The grains of all wires were refined by rolling and wire drawing, and the D value of the 0.2ECAP wire was the smallest of the three types of wires. Table 2 also summarizes the dislocation density, ρ_d , of the wires. The 0.2ECAP wire showed the highest value of ρ_d , while the 0.2IA wire showed the lowest value of ρ_d .

4. Discussion

4.1 Decrease in electrical conductivity by rolling and wire drawing

The electrical conductivity of alloys is affected by dislocation density, grain boundary density, and solute atom concentration. With increasing these values, the electrical conductivity becomes lower. It is generally known that the solute concentration in the Cu matrix has the greatest effect on electrical conductivity.⁷⁾ Therefore, in the present study, it can be considered that the increase of Zr solute atoms in the Cu matrix is the main reason of the decrease in electrical conductivity during rolling and wire drawing. Since the fcc precipitates have the cube-on-cube orientation relationship with the Cu matrix, it can be presumed that they are repeatedly cut by dislocations during rolling and wire drawing, resulting in dissolution of the fcc precipitates in the Cu matrix and a decrease in electrical conductivity of the wire. First, this presumption will be examined.

Figure 3(a) and (b) show the volume fractions, f , of the coherent fcc precipitates with certain ranges of radius as a function of the radius, r_c , of the fcc precipitates observed in the ECAP specimen and 0.6ECAP wire. The values of f were obtained from $(4/3)\pi r_c^3 N$, where N is the number density of the fcc precipitates with a certain range of radius per unit volume. The volumes were obtained by measuring the thickness of the TEM specimens using grain boundaries. A comparison of Fig. 3(a) and (b) reveals that all the f values of the fcc precipitates are reduced by rolling and wire drawing. In particular, the f values of the fcc precipitates with smaller radii were significantly decreased. These results indicate that the fcc precipitates were mechanically dissolved into the Cu matrix during rolling and wire drawing. Especially, the dissolution of the smaller fcc precipitates were significant.

Table 3 lists the volume fraction, f_c , and mean radius, $\bar{r}_c$, of the coherent fcc precipitates in the ECAP specimen, 0.6ECAP wire, A specimen, and 0.6A wire. Rolling and wire drawing of both ECAP and A specimens decreased the values of f_c and increased the values of $\bar{r}_c$. Thus, it is evident that the value of f_c was reduced due to mechanical dissolution of the smaller fcc precipitates more than the larger ones.

Table 3 also shows the resistivity, ρ , (the electrical conductivity, E), the dislocation density, ρ_d , the average intercept length, L , which is equivalent to grain size, and the amount of Zr solute atoms, C_{Zr} , of the ECAP specimen, 0.6ECAP wire, A specimen, 0.6A wire, IA specimen and 0.6IA wire. The values of C_{Zr} were calculated as follows.

The ρ value of each specimen can be expressed using ρ_0 , ρ_d , grain boundary density, S_v , and C_{Zr} as follows:⁸⁾

Fig. 3 Dependence of the volume fraction, f , of the fcc precipitates on radius, r_c , in (a) the ECAP specimen and (b) the 0.6ECAP wire.

Table 3 Volume fraction, f_c , and radius, $\bar{r}_c$, of the fcc precipitates, electrical resistivity, ρ , or electrical conductivity, E , indicated as $\rho(E)$, dislocation density, ρ_d , mean linear intercept length, L , and Zr concentration in the Cu matrix, C_{Zr} , for the ECAP specimen, 0.6ECAP wire, A specimen, 0.6A wire, IA specimen, and 0.6IA wire.

Specimen	f_c ($\times 10^{-3}$)	$\bar{r}_c$ (nm)	$\rho(E)$ (n Ω m (%IACS))	ρ_d ($\times 10^{15}$ m $^{-2}$)	L (μ m)	C_{Zr} ($\times 10^{-2}$ at%)
ECAP	6.4	3.6	19.5 (88.2)	0.2	0.9	1.6
0.6ECAP	4.3	4.6	23.4 (73.7)	1.5	0.5	4.6
A	10.9	5.6	19.4 (88.9)	-	13	1.9
0.6A	8.9	5.9	22.6 (76.3)	1.3	0.7	4.2
IA	-	-	18.5 (93.3)	-	4.7	1.1
0.6IA	-	-	19.0 (90.7)	1.2	1.3	1.1

$$\rho = \rho_0 + \Delta\rho_{dis} \cdot \rho_d + \Delta\rho_{gb} \cdot S_v + \Delta\rho_{Zr} \cdot C_{Zr}. \quad (1)$$

Here, S_v is given as $S_v = 2/L$.⁹⁾ Besides, the $\Delta\rho_{dis}$ and $\Delta\rho_{gb}$ are the contributions of dislocation density and grain boundary density to the resistivity, ρ , respectively. The theoretical values of $\Delta\rho_{dis} = 1.9 \times 10^{-16}$ n Ω m 3 and $\Delta\rho_{gb} = 2.1 \times 10^{-7}$ n Ω m 2 , reported by Karolik *et al.*,¹⁰⁾ were used. The $\Delta\rho_{Zr}$ is the amount of change in the resistivity when the Zr concentration increases by 1 at%. The value of $\Delta\rho_{Zr} = 110$ n Ω m/at% has been reported.¹¹⁾ The contribution of precipitates to the resistivity is assumed to be negligible.¹²⁾ The C_{Zr} value of each specimen was obtained by substituting these values of $\Delta\rho_{dis}$, $\Delta\rho_{gb}$, and $\Delta\rho_{Zr}$, as well as the values of ρ , ρ_d , and L shown in Table 3 into eq. (1).

Table 3 shows that, in both the ECAP and A specimens, C_{Zr} increases due to rolling and wire drawing, while f_c decreases. This confirms the dissolution of the fcc precipitates. In the 0.6ECAP specimen, the effect of dissolution of Zr atoms in the Cu matrix on the resistivity was found to be greatest. Specifically, the contributions of grain-boundary density, dislocation density, and Zr dissolution in the Cu matrix to the resistivity were 0.8 n Ω m, 0.3 n Ω m, and 5.1 n Ω m, respectively. The same tendency was observed in the A specimen. On the other hand, the C_{Zr} value of the IA specimen was lower than those of the ECAP and A specimens. Besides, it should be noted that the C_{Zr} value of the IA specimen did not change at all after wire drawing. This is because repeated intermediate annealing

allowed the precipitation to proceed sufficiently, making all the fcc precipitates incoherent, and as a result, the fcc precipitates were not sheared by dislocations during wire drawing. As a result, the electrical conductivities of the 0.2IA and 0.6IA wires are excellent at about 91%IACS.

4.2 Comparison of yield strengths

The yield strength of the 0.2ECAP wire was higher than those of the 0.2A and 0.2IA wires as shown in Table 1. The yield strengths of these wires are dominated by solid-solution strengthening, precipitation strengthening, grain-boundary strengthening, and dislocation strengthening. The C_{Zr} values for the 0.2ECAP, 0.2A, and 0.2IA wires calculated using eq. (1) are 4.7×10^{-2} , 4.3×10^{-2} , and 1.1×10^{-2} at%, respectively, which are extremely low. Therefore, the effect of solid-solution strengthening on the yield strength can be considered to be very low.

Next, the contributions of precipitation strengthening to the yield strengths of the 0.2ECAP, 0.2A, and 0.2IA wires are discussed. Although the data related to precipitation are available only for the wires with a diameter of $d = 0.6$ mm, it is considered that there is no significant difference in the volume fraction of the fcc precipitates between the wires with $d = 0.2$ mm and 0.6 mm for the following reason. The C_{Zr} values for the 0.6ECAP and 0.2ECAP wires are 4.6×10^{-2} and 4.7×10^{-2} at%, which are almost the same. Similarly, the difference in the amounts of Zr solute atoms between the 0.6A and 0.2A wires is also small, and there is no difference between the 0.6IA and 0.2IA wires. Therefore, it can be said that the volume fractions of the precipitates in the wires with $d = 0.2$ and 0.6 mm are the same. With this in mind, the precipitation strengthening in the 0.6ECAP, 0.6A, and 0.6IA wires are examined below.

Since dislocations cannot cut the incoherent fcc precipitates, it is easily imagined that the yield strength is dominated by the Orowan stress when only the incoherent precipitates are dispersed. Even in the A specimen in which the coherent fcc precipitates that can be cut by dislocation are dispersed, an annealing experiment after work hardening of the A specimen showed that the yield strength is dominated by the Orowan stress.¹³⁾ The Orowan stress is inversely proportional to the distance between precipitates, λ , and λ can be expressed by the following eq. (2):¹⁴⁾

$$\lambda = \bar{r}_s \{ (2\pi/3 f_s)^{1/2} - 1.63 \}, \quad (2)$$

where $\bar{r}_s$ and f_s are the average radius and volume fraction of the spherical precipitates. In the present study, $\bar{r}_s$ is the average radius, $\bar{r}_{ci}$, of the coherent and incoherent fcc precipitates, and the f_s is the sum of the volume fractions, f_{ci} , of the coherent and incoherent fcc precipitates. Table 2 shows the values of $\bar{r}_{ci}$, f_{ci} and calculated λ from eq. (2) for the 0.6ECAP, 0.6A and 0.6IA wires, respectively. Although there are slight differences in the λ values for these wires, it can be judged that the contribution of precipitation strengthening to the differences in yield strengths among the three wires is low. Therefore, it can be said that the differences in the yield strengths of the drawn wires are mainly caused by the differences in the amounts of dislocation strengthening and grain-boundary strengthening. In Tables 1 and 2, the highest yield strength of the 0.2ECAP wire is attributed to the smallest D and the highest ρ_d values. In contrast, the lowest yield strength of the 0.2IA wire was caused by the largest D and lowest ρ_d values.

4.3 Fabrication of an alloy with good strength, ductility, and electrical conductivity

The above results and discussions lead to two important points for producing alloy wires with good strength, ductility, and electrical conductivity. The first thing is to utilize recrystallization to change coherent fcc precipitates after sufficient precipitation into incoherent fcc precipitates. The second point is as follows. After finishing the process of obtaining incoherent fcc precipitates by recrystallization, a grain-refinement process such as severe plastic deformation processing, and final wire drawing are performed.

Phillips¹⁵⁾ has been reported that when a Cu–1.07Zr alloy was rolled and then aged at 500°C, no recrystallization occurred and Cu₅Zr precipitates were preferentially formed on dislocations. Therefore, after wire drawing of the cast alloy to $d = 5$ mm and introducing dislocations, the electrical conductivity, E , was increased to 90.6%IACS by preferentially precipitating Cu₅Zr on the dislocations through annealing at 500°C for 3 h. Then, annealing was performed at 650°C for 15 min in order to change the fcc precipitates and Cu₅Zr precipitates into incoherent ones by recrystallization. The recrystallized grain size after annealing was 7 μ m. Then, ECAP processing was performed for four times via route Bc¹⁶⁾ so as to improve the strength and ductility of the alloy by grain refinement. The grain size was decreased to 0.3 μ m. Finally, the wire drawing was carried out to $d = 0.2$ mm. This wire is referred to as 0.2IM wire. The grain size of the 0.2IM wire was decreased to 100 nm. As shown in Table 1, we obtained the 0.2IM wire with high values of $\sigma_u = 820$ MPa and $\varepsilon_t = 4.0\%$ while maintaining a high value of $E = 86.9\%$ IACS.

In the present study, we succeeded in fabricating wires with better balance of mechanical and electrical properties in laboratory-scale experiments. Our future challenges are how to incorporate the above mentioned process into an industrial-scale manufacturing process of wires.

5. Conclusions

- (1) The 0.2ECAP wire exhibited a 0.2% proof stress, $\sigma_{0.2}$, of 730 MPa and a tensile strength, σ_u , of 790 MPa. These values were higher than the ones of $\sigma_{0.2} = 650$ MPa and $\sigma_u = 710$ MPa of the 0.2A wire, and the values of $\sigma_{0.2} = 580$ MPa and $\sigma_u = 610$ MPa of the 0.2IA wire. The strength of the 0.2ECAP wire was the highest because the grain size was extremely refined to 120 nm and the dislocation density was the highest.
- (2) The electrical conductivities, E , of the 0.2ECAP and 0.2A wires were decreased from about 90%IACS to 73.0 and 74.1%IACS by rolling and wire drawing, respectively. This is because the ordered fcc precipitates, which were formed during casting process and newly found in the present study, were cut by dislocations and mechanically dissolved into the Cu matrix during wire drawing. On the other hand, the 0.2IA wire showed a high value of $E = 90.5\%$ IACS. This is due to the low concentration of Zr solute atoms in the Cu matrix caused by the sufficient precipitation process through the repeated intermediate annealing, and the fact that the fcc precipitates became incoherent by recrystallization and thus did not mechanically dissolve into the Cu matrix during wire drawing.
- (3) Based on the above mentioned findings in the wire-fabrication process, first of all, recrystallization was carried out to make the precipitates incoherent after sufficient precipitation process by annealing. After that, the ECAP process was incorporated followed by final wire drawing. As a result, an alloy wire with high strength, ductility, and electrical conductivity was able to be fabricated. The wire with a small grain size of 100 nm exhibited high values of $\sigma_u = 820$ MPa, $\varepsilon_t = 4.0\%$, and $E = 86.9\%$ IACS.

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